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SOME SURFACE EFFECTS ON GERMANIUM

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ELECTRICAL ENGINEERING RESEARCH LABORATORY
ENGINEERING EXPERIMENT STATION
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS


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Technical Report No. 2

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Prepared by:


**S. R. Morrison
Research Associate**

Approved by:


**John Bardeen
Professor**

**ELECTRICAL ENGINEERING RESEARCH LABORATORY
ENGINEERING EXPERIMENT STATION
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS**

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SOME SURFACE EFFECTS ON GERMANIUM

1. INTRODUCTION

1.1 Surface Traps

In 1947 Bardeen¹, in order to explain some contact potential measurements of Meyerhof² and others, found it necessary to postulate that there existed a space charge layer at the free surface of germanium and silicon.

This space charge layer arises from the trapping of electrons or holes at the surface of the material, a potential drop appearing between the charged surface and the oppositely charged interior.

There are three obvious types of surface traps. One possibility is the Tamm type trap. As the crystal is not periodic at the surface, the mathematics applied to the problem of an infinite crystal does not apply. When the mathematics is adjusted to take the surface into account, it indicates there may be allowed levels localized near the surface in the forbidden region of the energy level diagram. Traps arising in this manner are termed Tamm levels.

A second possible type of surface trap is the impurity atoms which for some reason are found in increased quantity near the surface. These impurities may be deposited during some surface treatment (etching, cutting, grinding) or may possibly deposit out from the bulk if the sample is heated.

A third type of surface trap is that arising from chemisorbed material on the surface. The chemisorption may require extraction of electrons from the germanium (as one would expect, for example, with chemisorbed oxygen), or a donation of electrons to the germanium (as one would expect with a strongly electropositive substance); or the chemisorbed material may be held by a bond which is in part homopolar, where one would expect that its role as a surface trap would depend on the fraction of the bond which is polar. These chemisorption traps are normally separated from the germanium by an oxide layer.

1.2 The Space Charge Region

The space charge layer, arising from trapping of holes or electrons in the surface traps, is a region where there is excess charge of opposite sign to that in the surface traps. For example, consider an N-type sample from which electrons have been trapped by the surface traps. These electrons will have been produced mainly by the donor impurities near the surface, and the region where these donor impurities have thus been left with a net positive charge is the space charge region.

The effect on the energy level diagram for the semiconductor in this example will be that the energy bands will rise near the surface, due to the potential change between the positive space charge region and

1. Bardeen, J. *Phys. Rev.* 71, 717, (1947).

2. Meyerhof, W. E.: *Phys. Rev.* 71, 727, (1947).

the negative surface states. If there is a negative surface charge on an N-type sample of germanium, the space charge region will extend to the order of 10^{-4} cm into the sample, as the electrons in the surface traps must come at least partially from the donor impurities in the material. If there is a positive surface charge on an N-type sample, the space charge region need extend only to the order of angstroms, as the electrons in this case will arise from the surface traps. For a P-type surface, the reverse considerations hold.

The problem of determining the charge trapped on surface states, and the space charge layer produced by this charge, is a self-consistent type of problem. For as charge is trapped on the surface, the energy bands at the surface shift with respect to the Fermi level, and the energy of the surface traps is changed. A more detailed analysis of this problem is presented by Bardeen¹.

Bardeen's analysis indicates the approach to the problem with respect to equilibrium between the growth of the space charge layer and the trapping of charge in surface traps. Morrison³ has investigated the case where equilibrium cannot be obtained. The space charge layer may act as a potential barrier separating the bulk semiconductor and the surface traps. If the temperature is too low for the charge to cross this potential barrier, interchange of charge between the surface traps and the bulk material is not possible and the equilibrium conditions are not attained. The results of the present investigation, as discussed below, indicate that at room temperature easy exchange of charge between the surface states and the bulk germanium occurs, and lower temperature is necessary to isolate the surface from the bulk.

The space charge region will affect the resistance of the sample, the contact potential, and many other surface properties.

The effect of the space charge layer on the contact potential, or the work function, is as follows. If the sample has a work function ϕ with no space charge layer, and if with a space charge layer the energy bands rise at the surface an amount eV_B , the work function will become $\phi + eV_B$.

The resistance of the sample will be affected owing to the fact that the shift of the energy bands near the surface with respect to the Fermi level means that the concentration of carriers in this region is different from that in the bulk semiconductor. This effect is discussed further below.

1.3 Methods of Investigation of the Surface

The separation of the effects of the three possible types of traps (discussed in Section 1.1) is a problem which has been attacked only partially. Brattain and Bardeen⁴, whose experiments will be discussed more fully later, separated the effect of the adsorbed ion traps from the effect of the impurity and Tamm traps by assuming that (a) a change of gaseous ambient surrounding the sample affects primarily the adsorbed

3. Morrison, R. University of Pennsylvania. Technical Report #4, Contract N6-onr-24914, (1952).

4. Brattain, W. H., and Bardeen, J. *E.S.T.J.* 32, 1, (1953).

ion traps, its effect on the other types being of a secondary nature, and (b) surface recombination depends solely on the impurity and Tamm traps. Using these criteria, they showed that on germanium there are at least two of the three types present, the adsorbed ions and one or both of the other types.

The effect of the surface traps may be measured by properties which depend on the space charge region and potential differences between the layers of surface traps. The contact potential of the material will depend on these voltages. The change in contact potential with light will depend to some extent on the complete surface condition, although it depends more directly on the impurity and Tamm traps, as is discussed by Brattain and Bardeen⁴. The resistance of the material will be a function of the space charge region, or to state the dependence more generally, will be a function of the charge removed from the material by the surface traps. The effect of an electric field on the resistance, the field being applied to the sample by using the sample as one plate of a "condenser" (the "field effect"), will also depend on the surface condition.

1.4 Contact Potential and Change in Contact Potential with Light

Brattain and Bardeen⁴ measured the effect of ambient atmosphere upon the first two properties listed above, the contact potential of germanium with respect to platinum, and the change in contact potential with light.

They found that gases with the hydroxide radical produced one extreme in the contact potential, and gases containing active oxygen (ozone, peroxides) produced the opposite extreme.

The contact potential can be expressed as follows:

$$c.p. = -V_B - V_D + \text{const}$$

where V_B is the potential drop across the space charge layer, V_D is the potential drop between the adsorption traps and the Tamm or impurity traps. Brattain and Bardeen found that the effect of the hydroxide radical was to increase the contact potential, or to decrease the work function of the germanium. The effect of active oxygen was the reverse. Thus hydroxide ions make the surface more positive, active oxygen makes the surface more negative.

The change in contact potential with light is due to the fact that when light falls on the samples, electrons and holes are produced, and these excess carriers upset the equilibrium conditions in the impurity or Tamm traps. This in general will change the net charge on the surface, thus changing the contact potential. Brattain and Bardeen found that the change in contact potential with light, $(\Delta c.p.)_L$, was a function of the contact potential.

1.5 Resistance and Field Effect.

This work was started to measure the effect of ambient atmosphere on the third property mentioned above, the resistance of the germanium

The effect to be expected is as follows. If the net charge on the surface changes, the potential drop between the space charge and the surface charge will change. This means the energy bands near the surface will either rise or fall with respect to the Fermi level. Thus the surface resistance will change.

For an N-type sample, there are three possible surface conditions, two of which are shown in Fig. 3. First, as is shown in 3(a), if there is a strongly negative surface, so that at the surface the valence band is closer to the Fermi level than the conduction band, one will have an "inversion layer", a P-type region on the surface of an N-type sample. This surface condition, where there is an abnormally high hole conductivity near the surface, will be denoted as a π -type surface. A second possible surface condition is that shown in Fig. 3(b). If there is a positive charge in the surface states, the bands will bend down near the surface, and there will be an abnormally high electron conductivity near the surface. A surface condition with an abnormally high (higher than in the bulk semiconductor) electron conductivity will be denoted as a ν -type surface. A third possible surface condition is of the Schottky type, with an exhaustion region (region where the conductivity is low) near the surface. If on an N-type sample there is a negative charge on the surface states, but not sufficient to produce a π -type surface, then the bands will rise at the surface with respect to the Fermi level, leaving a region with a depleted number of conduction electrons.

A similar array of three possible surface conditions exists for a P-type sample. For an intrinsic sample, of course, there are only the two possible types, the π -type and the ν -type surfaces.

The effect of a variation in the surface states' charge on the resistance of the sample will be as follows. If the energy bands are lowered at the surface, there will be a decrease in the number of holes and an increase in the number of electrons. So if the surface is ν -type, the resistance will decrease, if the surface is π -type, the resistance will increase. If the surface is Schottky type, the change in resistance will depend upon whether the sample is N- or P-type, decreasing for N-type, increasing for P-type.

The fourth method of investigating the surface discussed in Section 1.4, is the effect of an electric field on the resistance. If one uses the sample as the negative plate of the "condenser", this will lower the energy bands near the surface. If the surface is ν -type, the resistance will decrease, and so on. This may then be used as an independent check upon the simple resistivity measurements in indicating the type of surface. Preliminary work on this field effect measurement has been done, and checks with the resistance measurements.

2. APPARATUS

Measurements of the resistance, the change in contact potential with light, the photoconductivity, and the field effect as functions of the ambient atmosphere have been made on germanium at NTP.

The resistance measurements were made for reasons discussed in the preceding section. As the resistance changes to be measured were very small, all temperature fluctuations had to be eliminated. This was accomplished to a reasonable extent by putting the sample container in a Dewar filled with water at room temperature, which acted as a heat reservoir. The gas flowing over the sample was passed through a copper coil immersed in the water to allow it to come to the correct temperature before reaching the sample. The resistance was measured using the potentiometer probe method.

The change in contact potential with light was measured by using a platinum screen close to the germanium as a reference electrode, and by shining chopped light (170 cps) on the sample. The contact potential between the platinum and the germanium thus changed at 170 cps, yielding an AC voltage across the "condenser" which could be amplified and measured.

This measurement was made in order to correlate this work with that of Brattain and Bardeen⁴. From their simultaneous measurements of $c.p.$ and $(\Delta c.p.)_L$, it was possible to assume how the $c.p.$ was varying in our samples from our $(\Delta c.p.)_L$ measurements.

The photoconductivity was measured by passing a constant current through the sample and measuring the AC voltage produced by the chopped light. This measurement was made to give an idea of how the lifetime of the minority carriers in the sample was changing as a function of ambient. Changes in the photoconductivity were assumed due to changes in the lifetime.

The preliminary measurements on the field effect have been made by using as one plate of the "condenser" the same platinum screen used in the $(\Delta c.p.)_L$ measurements. The reason for this measurement is discussed in the preceding section.

The surface condition varied during these measurements was the ambient atmosphere, which was cycled between wet and dry oxygen. These atmospheres have been used in order that the results can be compared with Brattain and Bardeen's directly.

3 RESULTS AND INTERPRETATION

In Fig. 1 are shown typical results for an N-type sample. At time zero the ambient atmosphere is changed from dry to wet oxygen, and the resistance of the sample decreases. From comparison of the measurements of $(\Delta c.p.)_L$ with those of Brattain and Bardeen, it is found that the energy bands near the surface are lowering. As the resistance decreases while the energy bands lower, a ν -type or a Schottky type surface is indicated. The useful properties of the sample are given in Table I.

Also indicated in Fig. 1 is the variation of photoconductivity with ambient. Brattain and Bardeen found that the lifetime of the samples is constant under the wet to dry oxygen treatment. We have found that the change is not necessarily zero, but averages 5 to 10%, sometimes no change occurring within the 5% probable error of our measurements, and once a change of 40% occurring.

TABLE I

Sample	Resistivity (ohm cm)	Cross-section	Thickness (cm)
N-A	5.8	square	0.054
P-A	12	square	0.10
N-B	47	rectangular	0.04
P-B	26	rectangular	0.067
N-D	26	rectangular	0.045

Figure 2 is a similar typical curve for a P-type sample. Here again the $(\Delta c.p.)_L$ measurement indicates that the energy bands are lowering at the surface. As the resistance increases, this indicates a ν -type or Schottky type surface.

On a P-type sample of germanium, a ν -type surface has not as yet been observed, but for an N-type sample, π -type surfaces have been observed, as is shown in Fig. 4 and some of the following figures. As yet it has not been discovered why, with apparently identical surface treatment, (CP₄ etch), the surface of an N-type sample sometimes is π -type, sometimes ν - or Schottky type.

In Fig. 4 are shown some operations performed on an N-type sample which had a π -type surface after etching. It was possible by heating the sample to change the surface to Schottky or ν -type, and by cooling the sample to reduce the net surface changes. Further development of this empirical technique may be of interest, since a sample whose

surface resistance is not affected by ambient atmosphere is desirable in germanium diode and triode applications

As the sample becomes "aged", i.e., as the sample is left for the order of days after etching, the resistance measurements obtained during gas cycling become less monotonic, as in Figs. 1 and 2, and extra maxima and minima appear. Little consistency in these effects from sample to sample, or even from etching to etching, has been observed. The only effect of this type which has reappeared to the extent of being recognizable is the one shown in Fig. 5. For a P-type sample, one sometimes observes an extra minimum during the water vapour half of the gas cycle, and an extra maximum during the dry oxygen half. These extra maxima and minima increase with time, the curve shown in Fig. 5 being quite early in the "ageing" process.

Another effect observed in "ageing" the sample is a net decrease in the total change in the resistance of the sample with gas. This effect is demonstrated in Fig. 6. This may be explained by the growth of an oxide layer on the germanium, making the adsorption states farther away from the surface, hence less effective in changing the resistance of the germanium.

Parenthetically it may be noted that the curves of Fig. 6 indicated that this N-type sample has a strong π -type surface. In Fig. 7 are shown curves for the same N-type sample following another etching, when the sample has a strong ν -type or Schottky surface.

On samples which are close to intrinsic, the type of curve as shown in Figs. 8 and 9 are observed. Here the resistance goes through a maximum in both the wet and dry oxygen periods of the cycling. A possible explanation of this is as follows. If an N-type sample has a π -type surface (conduction by holes at the surface) and water vapour is applied, bending the bands down at the surface, it is conceivable that the bands may lower until the Fermi level is about midway between the bands (an "intrinsic" surface). This will give the maximum possible resistance, and if the bands continue down further, the resistance will drop, as the surface is now Schottky type. A similar picture is possible for the P-type sample.

Of course if this analysis is valid one would expect the maximum resistance to be equal for the wet oxygen and the dry oxygen parts of the curve, which they do not appear to be. Field effect measurements have not as yet been performed on these samples.

4 DISCUSSION

This work provides further evidence that a space charge layer does exist at the free surface of a semiconductor. The correlation between the resistance of the material and the $(\Delta c.p.)_L$ indicates that resistance changes are associated with changes in the barrier height with ambient atmosphere.

The number of charge carriers per unit area which must be introduced into the crystals to produce the observed change in resistance with ambient can be calculated to be $\delta N = \frac{n_0 W}{4} \frac{\delta B}{R}$, where R is the

resistance, n_0 is the equilibrium concentration in the interior, and W is the thickness of the square filament. From the typical data included, $\delta N = 4 \times 10^{10}/\text{cm}^2$ for both the N-type and the P-type crystals. Since carriers near the surface may have mobilities which are smaller than normal, the actual values of δN may be larger than given by this estimate.

It is of interest to estimate the minimum thickness of the space charge layer which will account for the results obtained.

The results shown in Fig. 1 indicate that the resistance is decreasing as V_B decreases. This indicates that the N-type sample is ν -type or Schottky type at the surface. Using the theory for the Schottky type surface, letting σ be the measured conductivity, σ_0 the conductivity if there were no space charge layer, and x_0 the thickness of the space charge layer, then

$$\sigma = \sigma_0 \left(1 - \frac{4x_0}{W}\right)$$

where W is the thickness of the square crystal.

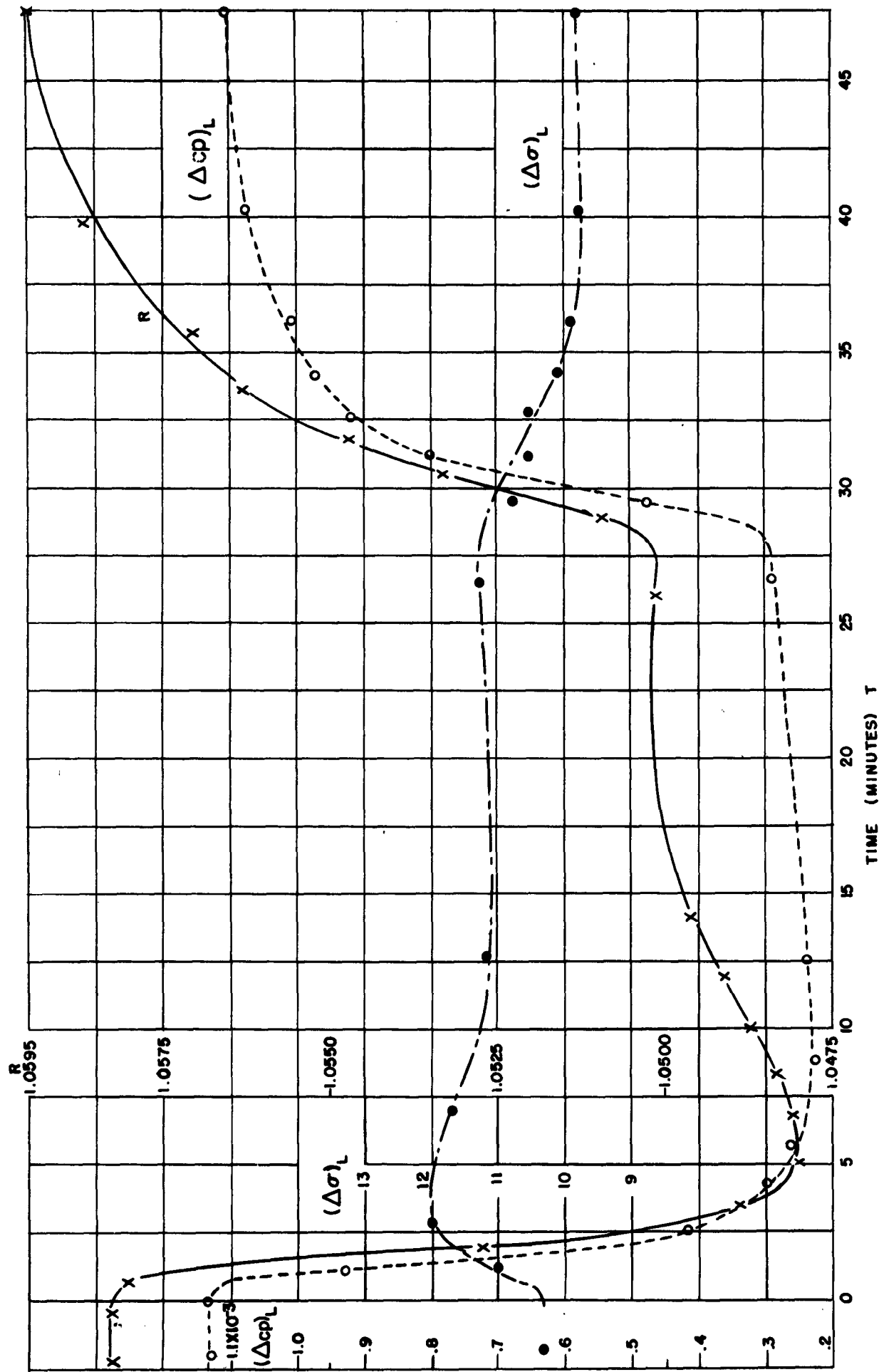
$\frac{\delta \sigma}{\sigma_0}$ has been measured to be up to 0.01 for $W = 0.05$ cm. Hence $\delta x_0 = \frac{0.05 \times 0.01}{4} = 10^{-4}$ cm is the range through which x_0 has change, and thus $x_{0 \text{ max}}$, the value of x_0 for highest resistivity, is at least 10^{-4} cm. The Schottky barrier layer theory, using, in MKS units, $V_B = eN_0 x_0^2 / 2K$ (where N_0 is the impurity concentration, K the dielectric constant), yields a minimum value for V_B of 0.25 volts when the sample is at its highest resistivity.

The calculations of Brattain and Bardeen indicate that the change in V_B while going from O_2 to H_2O is less than 0.1 volts. So the assumption above, leading to changes in V_B of the order of 0.25 volts, must be poor. The questionable assumption is that at all times we are dealing with a Schottky type surface. If the surface becomes ν -type,

large changes in the number of charge carriers can occur with small changes in V_B .

The work above describes only a preliminary investigation into a phenomenon which, it is expected, will provide a simple and useful tool for studying surface properties. The phenomenon is also important in applications, as the effect of atmosphere on the surface resistivity is important for transistors. If there is a π -type surface on the N region of a PNP transistor, it will act as an easy path for the flow of holes from the emitter to the collector and reduce the efficiency of the transistor.

ILLUSTRATIONS



Sample in Dry O_2 to $t = 0$
 in Wet O_2 to $t = 26$ Min.
 in Dry O_2 to $t = 48$ Min.

FIGURE 1

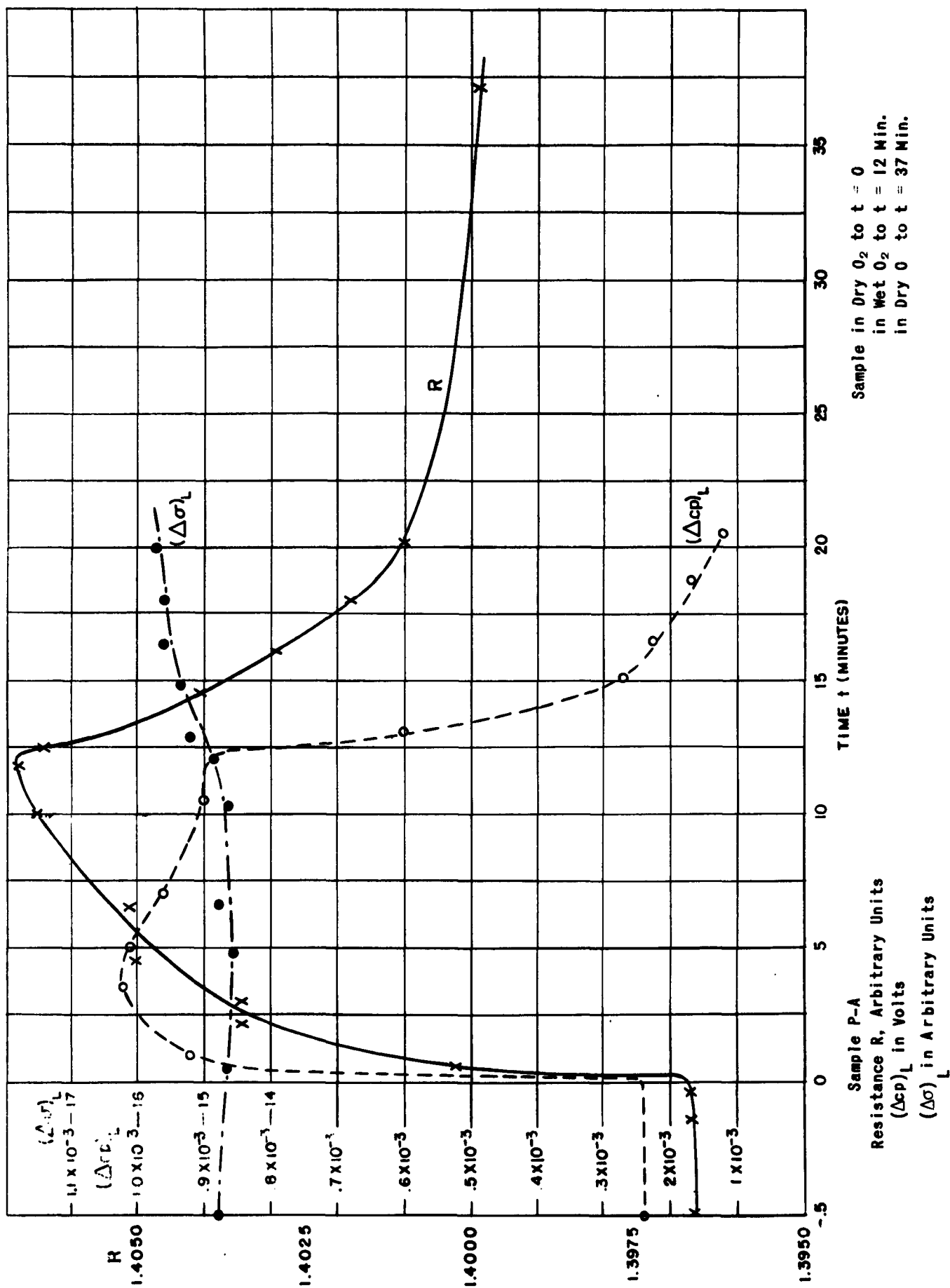
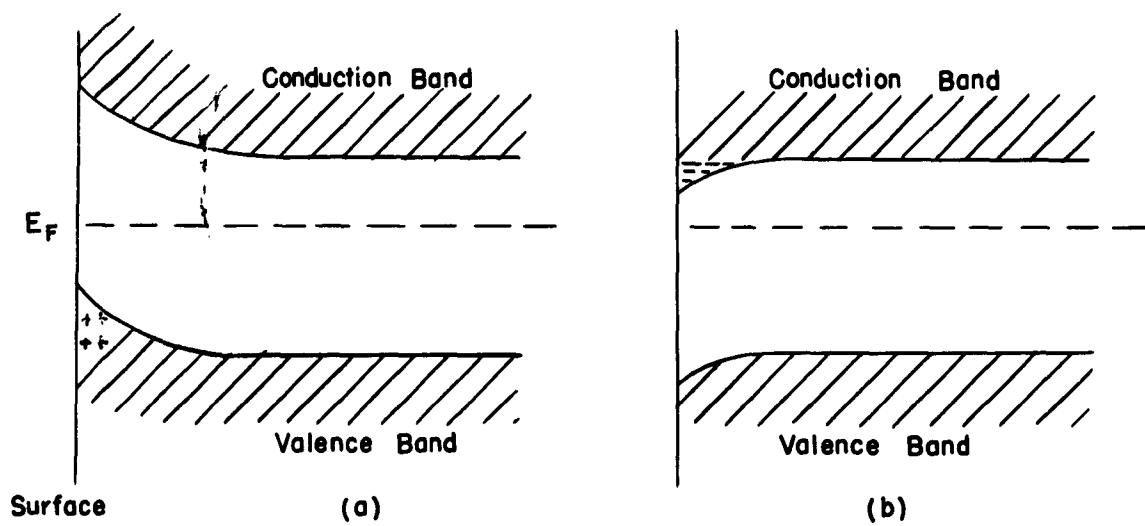


FIGURE 2

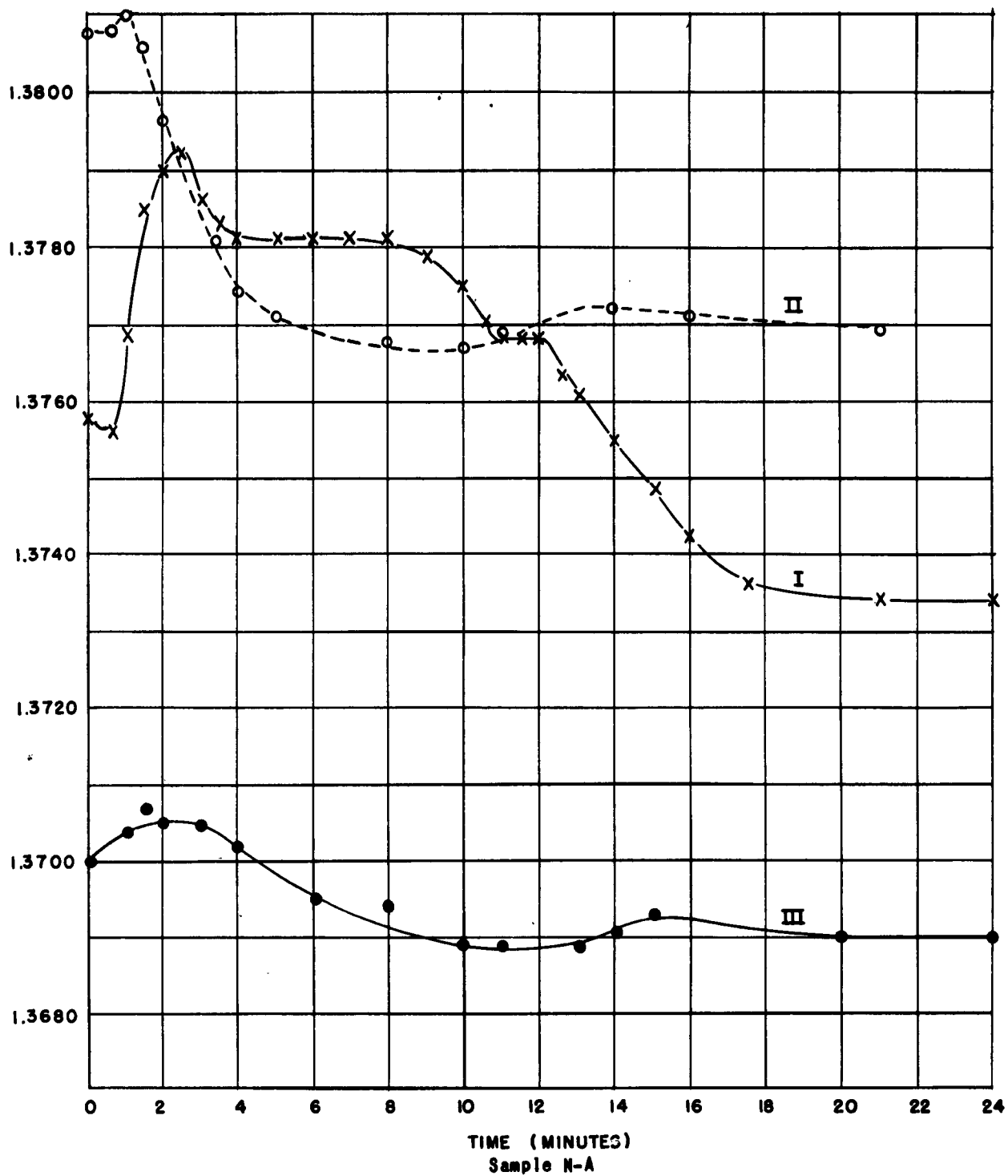


Possible Energy Band Structure at the Surface, for an N-Type Sample

(a) Surface P-Type

(b) Surface Strongly N-Type

FIGURE 3



Curve I Taken After Etching Sample
 Curve II Taken After Heating Sample to 70° C for 5-Min.
 Curve III Taken After Cooling Sample to 0° C for 20 Min.
 Sample in Wet Oxygen From T = 0 to T = 10 Min.
 in Dry Oxygen From T = 10 to T = 25 Min.

FIGURE 4

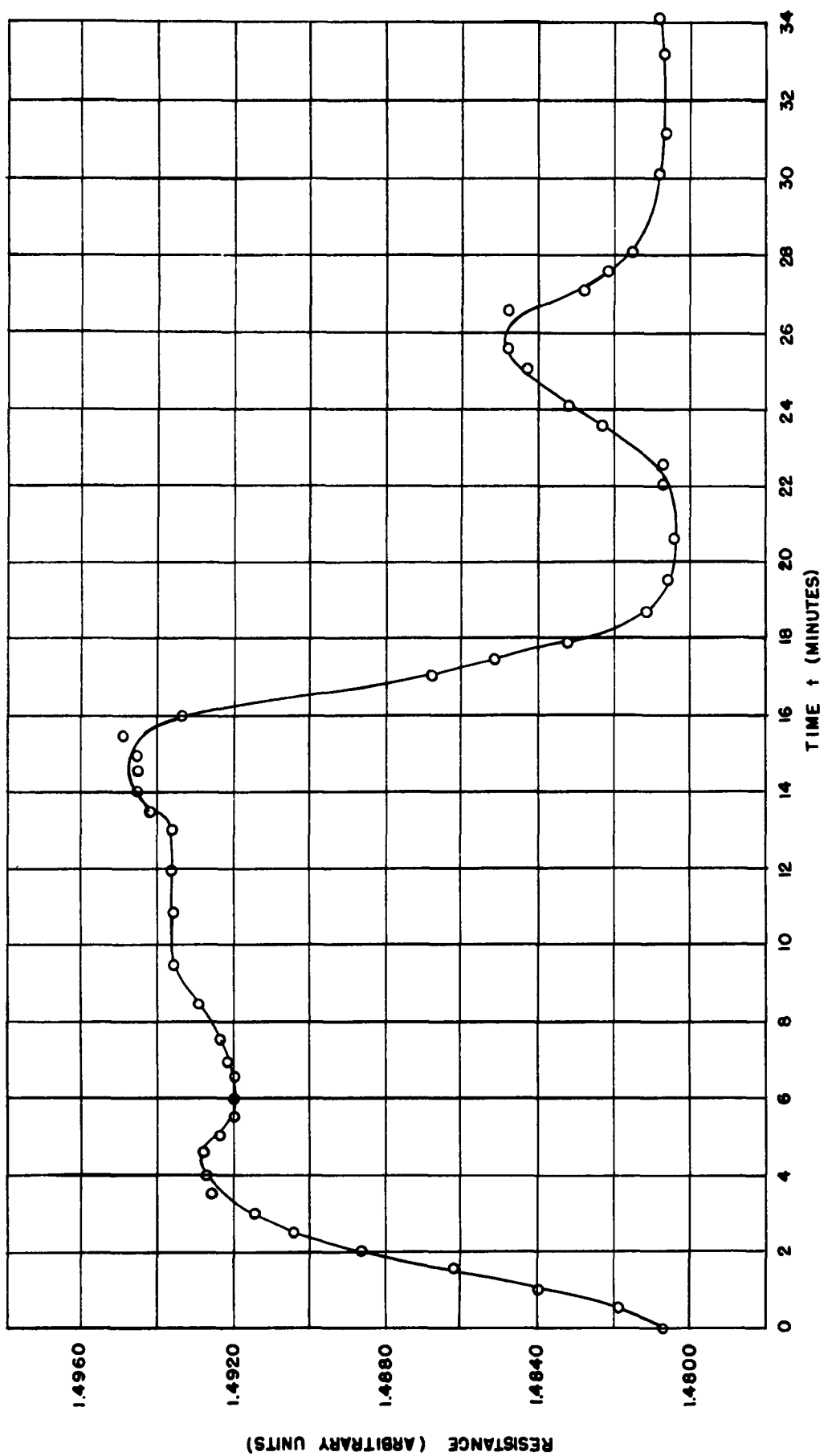


FIGURE 5

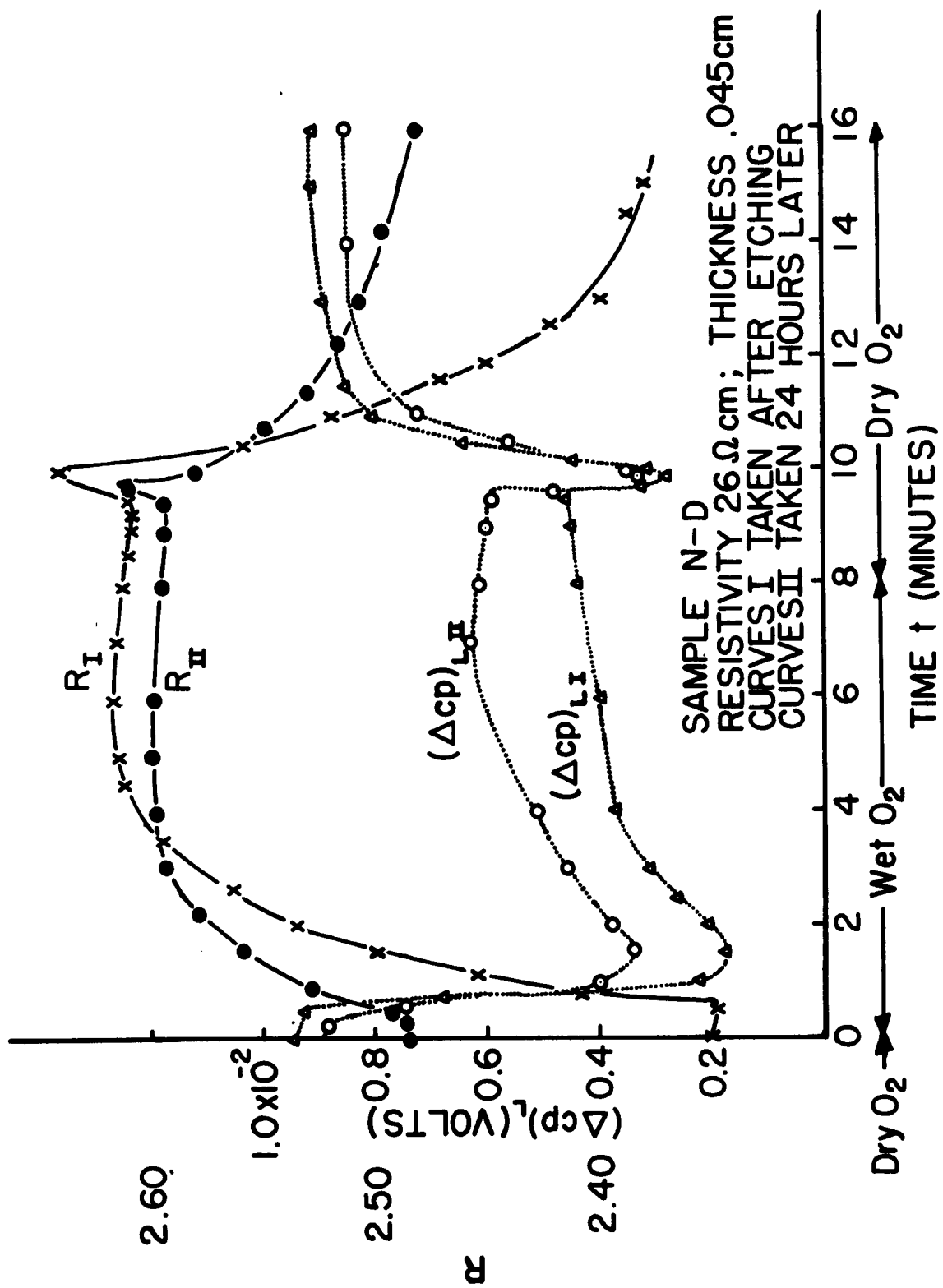


FIGURE -6

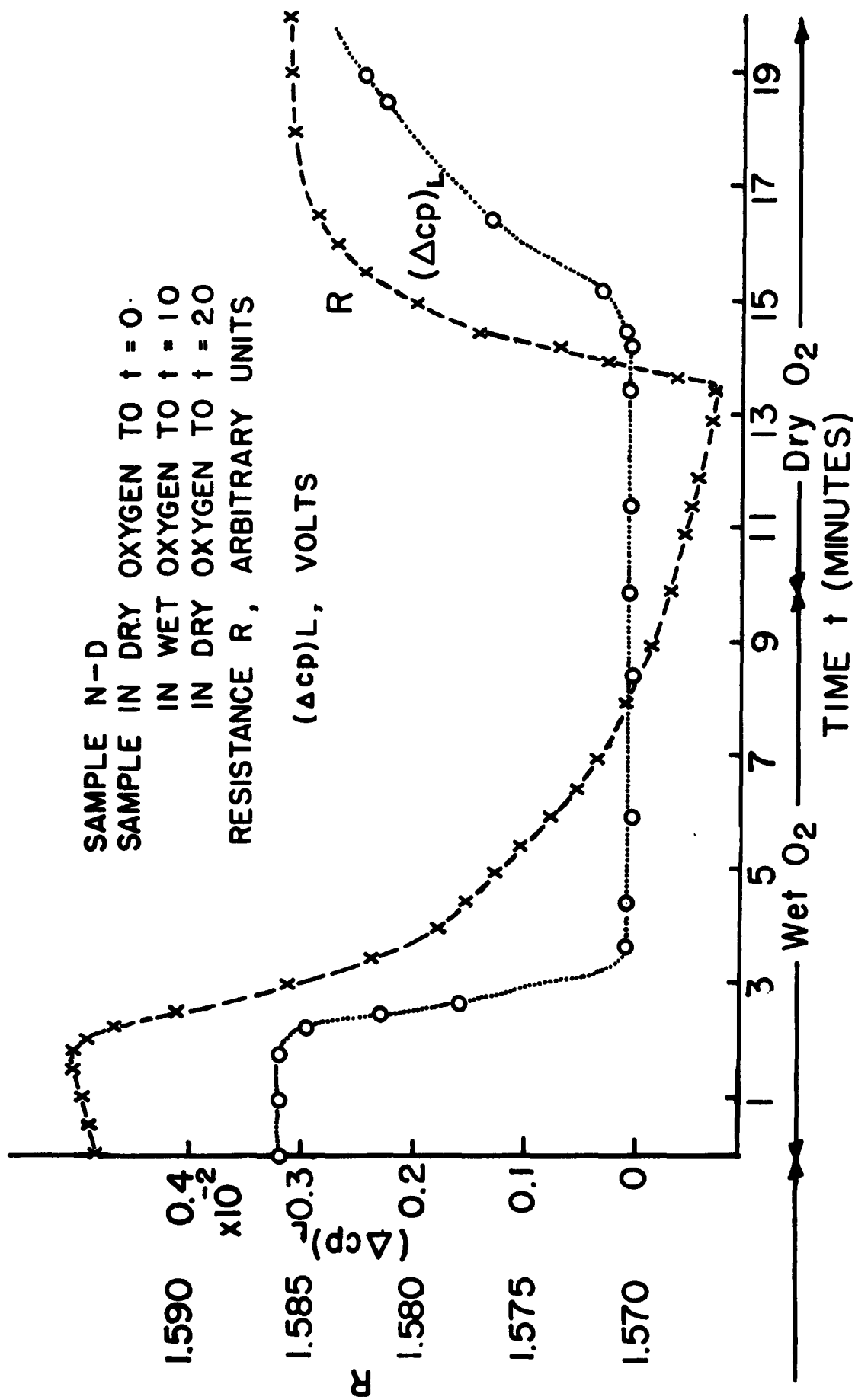


FIGURE -7

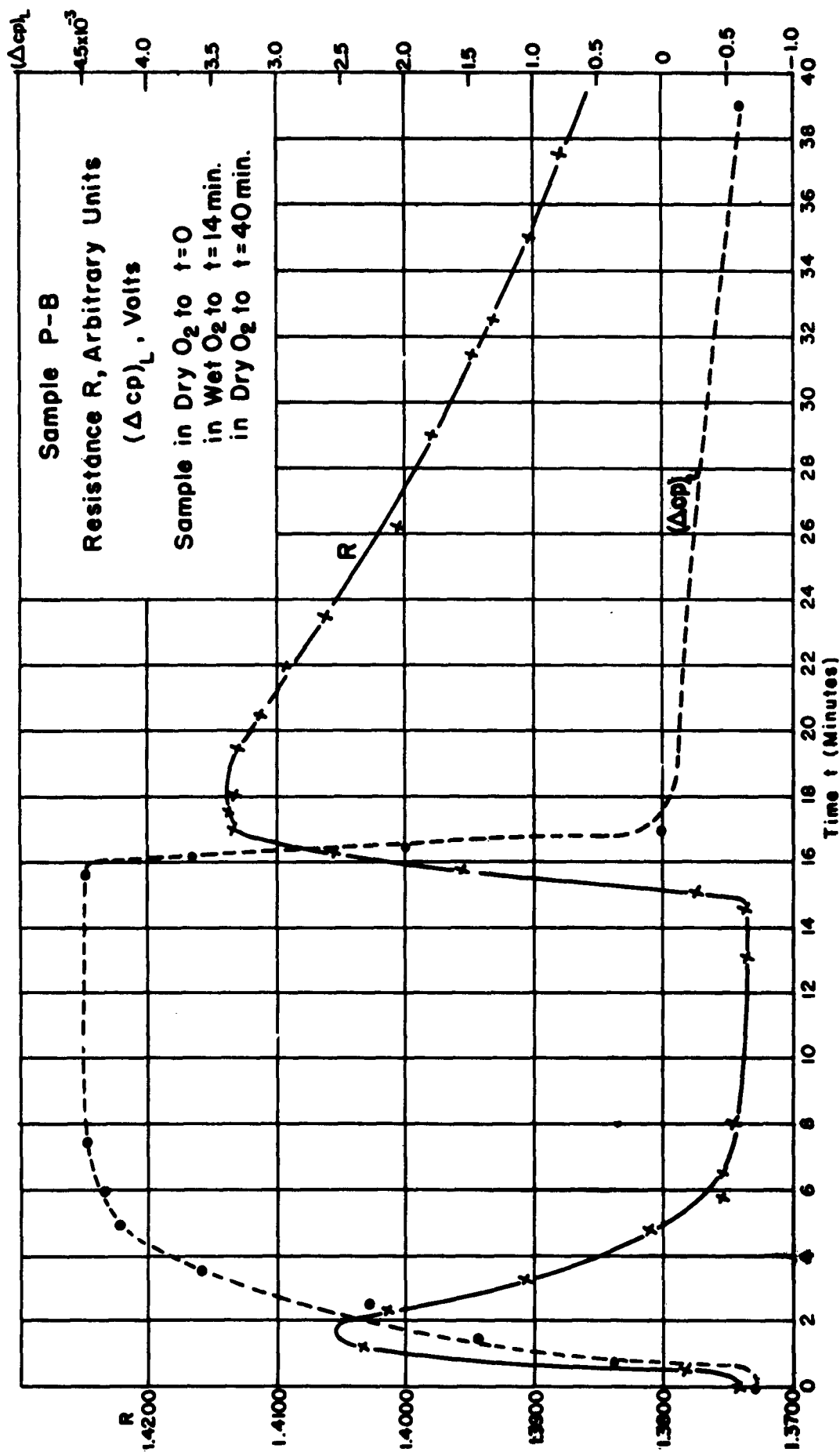


FIGURE - 8

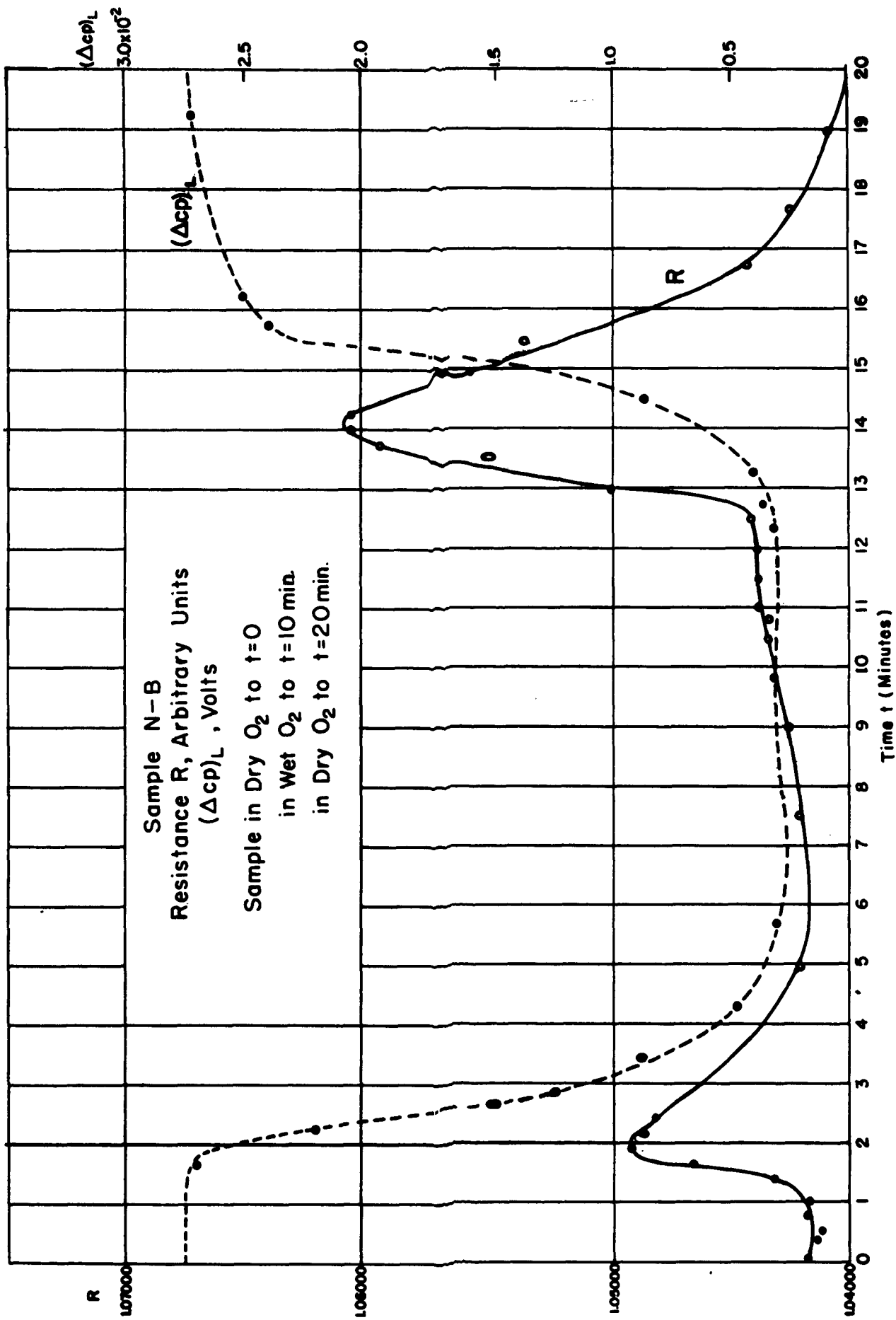


FIGURE - 9